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Experimental study of the aqueous CO₂-NH₃ rate of reaction for temperatures from 15°C to 35°C, NH₃ concentrations from 5% to 15% and CO₂ loadings from 0.2 to 0.6.

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Keywords:

- CO₂ capture
- Kinetic
- Rate of absorption
- Ammonia
- Mass transfer
- Experimental measurements

Highlights:

- Study on the kinetic of CO₂ absorption by NH₃ solvents at plant conditions
- Study of the Temperature, NH₃ concentration and CO₂ load dependence on K_{ov}
- Modelling of the reactor and kinetic constant calculation
- Error analysis and data fitting with the kinetic model
- Kinetic model fits data from literature in a wide concentration range

Abstract:

The absorption reaction between aqueous NH₃ and CO₂ was studied using the Wetted Wall Column. A total of 27 different cases are investigated in the region defined by temperatures from 15°C to 35°C, NH₃ concentrations from 5% to 15%, which are the typical solvent conditions in absorption columns, and

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lastly CO₂ loadings from 0.2 to 0.6. The resulting overall mass transfer coefficient of absorption measured follows the trends described by the modelling of the reactor and the equations used to describe the rate of the absorption reactions. Moreover, the overall mass transfer coefficient of absorption is in agreement with data available in the literature, valid in smaller portions of the investigated region. From the data analysis, the kinetics of the absorption reactions in the liquid phase is characterized. The equation proposed to fit the data is a power law equation which reproduces the experimental results measured at different CO₂ loadings. This represents a novelty because in literature the kinetic model of the reaction is usually fitted only to data for unloaded solutions (CO₂ loading equal to zero). Hence, in this case there is an experimental evidence that the kinetic model holds true in every loading conditions. The kinetic model intercept the values found in literature in every range of concentration. Consequently, the model is valid in every conditions and the rate of the reaction between NH₃ and CO₂ in liquid phase is described with an Arrhenius constant with a pre-exponential factor of $1.41 \cdot 10^8$ [mol/(m³s)] and an activation energy of 60680 [J/mol], a linear dependence on the CO₂ concentration and a dependence on the NH₃ with an exponent $\gamma = 1.89$. The proposed equation is found to be appropriate for implementation into process simulation software.

1. Introduction

The greenhouse gas effect associated with anthropogenic carbon dioxide emissions in the atmosphere is considered by many institutions the main cause of the global warming. One of the most mature technologies for CO₂ capture at the point of emission is the solvent-based chemical absorption/desorption process (Nielsen and Richard, 1997)(Rochelle, 2011). For physical absorption, the mass transfer is only dependent on the solubility and diffusivity of the absorbed compound in the solvent. In chemical absorption the solvent also reacts with the absorbed compound (carbon dioxide) enhancing greatly the mass transfer rate. Hence, a fast reaction rate for chemical solvents allows an equipment with smaller

sizes and lower costs (Valenti et al., 2012). In other words, the capital costs of capture plants can be lowered by reducing the size of the CO₂ capture equipment, which can be accomplished by intensifying the mass transfer of CO₂ with fast reacting solvents. The operational costs can be reduced by lowering the thermal energy needed for the desorption step, which is responsible for over 50% of the total energy requirement of the process (Svendsen et al., 2011).

Aqueous ammonia is reported as a promising technology for the CO₂ absorption by many works in literature (Valenti et al., 2012)(Svendsen et al., 2011)(Bai and Yeh, 1997)(Darde et al., 2012)(Lillia et al., 2016)(B R W Pinsent et al., 1956)(Wang et al., 2011)(Li et al., 2015). Ammonia technology is promising especially for the energy consumptions due to the high CO₂ loading achievable by the solvent and the low heat of desorption in the regenerator (simulations with an equilibrium base approach show an heat duty of 2.19 MJ/kgCO₂ and a SPECCA of 2.58 MJ/kgCO₂ (Bonalmi et al., 2016). Moreover, ammonia is chemically stable, has low costs and has not degradation carcinogenic products like happened for the amines. An accurate study of the kinetics of the absorption can help the evaluation of the correct size of the columns and the optimal configuration of fluxes in the capture plant in order to minimize the capital and energetic costs. A few works proposing models for the kinetic constants of the absorption reaction between aqueous ammonia and CO₂ are found in the open literature. Unfortunately, the published kinetic models are not in agreement with each other as showed by Lillia *et al.* (Lillia et al., 2016).

This work is divided in two parts: First, the experimental study of the absorption reaction between aqueous NH₃ and CO₂ using the Wetted Wall Column technique is described. The experiments are designed in order to determine the overall behavior of the absorption rate with respect to the temperature, the ammonia concentration and the CO₂ loading in the typical operative conditions of a capture plant.

Next, the overall mass transfer coefficient is analyzed and a kinetic model of the aqueous reaction between the ammonia and CO_2 is determined on the basis of the experimental data.

The goal is to implement a precise kinetic model in process simulation software, such as Aspen Plus. Then simulations can be carried out to quantify the effect of the absorption kinetic on the column size and the overall plant design. Therefore, the equation proposed for the kinetic constant is a power law, which is commonly used in codes. Furthermore, all the data measured at different CO_2 loadings are fitted by the kinetic model. This fact represents a novelty because in literature the kinetic model of the reaction is usually fitted only to data for unloaded solutions (CO_2 loading equal to zero) (B R W Pinsent et al., 1956)(Wang et al., 2011)(Darde et al., 2011)(Puxty et al., 2010). This approach gives a better comprehension of the kinetic behavior of the reaction in operative condition close to the absorption condition of a real absorption column. Indeed, the unloaded solution does not have the full ionic speciation in liquid phase, hence the experimental data of the CO_2 absorption are not influenced by the all the ions that are usually present in the liquid phase. Since in an absorption column the solvent is always loaded by the CO_2 , the data at different CO_2 loading can provide an evidence whether the rate of reaction is influenced by the speciation or depends only by the concentration of the reagents.

The reaction between ammonia and carbon dioxide is involved also in other industrial processes, like the production of fertilizers to name a very important one. Also in these processes, a better knowledge of the kinetic of the reactions helps the improved design and the reduced cost of the equipment and the whole plant optimization (Buckingham et al., 1986).

2. Measurement of CO₂ absorption rate

The experimental apparatus chosen for the measurement of the CO₂ absorption rate is the Wetted Wall Column (WWC). The configuration of the WWC is very simple and can reproduce in a good scale the simulation of the mass transfer of a real packed column. The results permit understanding the overall phenomenon and recognizing the operational parameters, which are more influent on the CO₂ absorption. The WWC used in this work is the WWC developed by Darde *et al.* (Darde et al., 2011). This equipment was also used by Paul and Thomsen (Paul and Thomsen, 2012) and by Gladis *et al.* (Gladis et al., 2017). The experimental apparatus is therefore well tested and well maintained. Hence, the reliability of the apparatus and the measurements are high.

2.1. Wetted Wall Column (WWC) experimental apparatus

Figure 1 shows the experimental apparatus used in this work. It allows for counter-current contact between the liquid solvent and a defined gas mixture. CO₂ and N₂ are supplied by gas bottles with a mole flow controlled by two Bronkhorst mass flow controllers which determine the composition of the inlet mixture in the chamber. The gas is saturated before the reaction chamber at the same temperature chosen inside the reactor chamber for the experiment. Between the reaction chamber and the CO₂ concentration probe is positioned a condenser. The saturators and the condenser are necessary in order to have the gas with relative humidity of 100% and consequently determine accurately the amount of CO₂ in the gas flow. Before the reaction chamber, in the gas line, there is a bypass valve. The valve allows to measure the carbon dioxide concentration before and after the absorption reactions switching the flow straight to the CO₂ probe or to the reaction chamber.

The thermostatic bath controls the temperature of the reaction chamber and the temperature of the inlet solvent in the reaction chamber. The solvent, prepared with a known NH₃ concentration and CO₂ loading,

117 is pumped into the thermostatic bath and then into the reaction chamber. The reaction chamber consists
 118 of a glass tube in which a stainless steel tube is located (dimensions are reported in Figure 1). The liquid,
 119 pushed inside the stainless steel tube, falls down in a thin film around the stainless steel tube. In this way
 120 the contact area between the liquid and the gas phase is well defined.

121

122 Based on the known contact area between the gas and the liquid, and the amount of CO₂ absorbed in the
 123 chamber, it is possible to determine the dependence between the CO₂ surface flux absorbed by the liquid
 124 and the CO₂ concentration in the gas mixture at a fixed temperature. The methodology used to prepare
 125 the solvent, the experimental procedure and all the data measured are reported in the article by Lillia *et*
 126 *al.* (Lillia et al., n.d.).

127

128

129 **Figure 1.** Wetted Wall Column layout where: (i) solid blue line is the solvent, (ii) dashed red line is the
 130 gas mixture and (iii) dotted black line the cooling water from the thermostatic bath (Gladis et al., 2017).

131 2.2. Definition and measurement of the overall mass transfer constant

132 The CO₂ concentration of the gas is measured at the inlet and the outlet of the reactor. Knowing the CO₂
 133 concentration before the reactor, after the reactor, and the amount of water in saturated condition, the
 134 mole flow of absorbed CO₂, ΔN_{CO_2} [mol/s], is calculated as

$$\Delta N_{CO_2} = \frac{N_{inert}(y_{CO_2}^{bypass} - y_{CO_2}^{WWC})}{(1 - y_{CO_2}^{bypass})(1 - y_{CO_2}^{WWC})} \quad (1)$$

135 from the molar flow of inert compounds (N₂ and H₂O), N_{inert} [mol/s], determined as

$$N_{inert} = N_{N_2} + (N_{N_2} + N_{CO_2}) \frac{\frac{P_{H_2O}^{WWC}}{P_{TOT}^{WWC}}}{1 - \frac{P_{H_2O}^{WWC}}{P_{TOT}^{WWC}}} \quad (2)$$

136 where $y_{CO_2}^{bypass}$ [-] is the mole fraction in the bypass, $y_{CO_2}^{WWC}$ [-] the mole fraction after the reactor, $P_{H_2O}^{WWC}$
 137 [Pa] the saturation pressure of the water in the reactor, P_{TOT}^{WWC} [Pa] the pressure in the reactor, N_{N_2} [mol/s]
 138 the mole flow of N₂ and N_{CO_2} [mol/s] the mole flow of CO₂.

139

140 The CO₂ probe measures the volumetric concentration of CO₂ for standard conditions (298.15 K,
 141 101325 Pa), so the CO₂ reading is corrected according to an application note from Vaisala (slightly
 142 changed to match the units used in this work):

$$y_{CO_2}(T, P) = y_{CO_2}(298.15 K, 101325 Pa) \frac{P [Pa]}{101325 Pa} \frac{298.15 K}{T[K]} \quad (3)$$

143 where T [K] and P [Pa] are the environmental conditions in the laboratory.

144

145 The measurement of the interface area between the liquid and the gas phase is important in order to know
 146 the surface flow of CO₂ in the liquid. The mass transfer area can be calculated knowing the geometry of
 147 the wetted cylinder and the liquid film thickness. The liquid film thickness, δ_{film} [m], is computed

148 according to the equation from Bird *et al.* (B. Bird, W. E. Stewart, 2000) based on the momentum balance
 149 expressed as

$$\delta_{film} = \sqrt[3]{\frac{3\mu_L V_{liq}}{\rho_L g L}} \quad (4)$$

150 where V_{liq} is the volume flow of the liquid [m³/s], L the column length [m], g is the gravity acceleration
 151 [m/s²], μ_L [Pa s] is the viscosity and ρ_L [kg/m³] is the density of the liquid at the reaction condition. Their
 152 value of the density and viscosity are measured with the densimeter and the microviscometer described
 153 by Lillia *et al.* (Lillia et al., n.d.). The total mass flow area is the area of the cylinder made by the liquid
 154 film. Its surface is computed adding at the diameter two times the liquid film thickness and adding one
 155 time the film thickness to the height of the cylinder considering also the surface of the top part, where
 156 the liquid flows out. The area at the interface A_{int} [m²] is computed as

$$A_{int} = \pi(2\delta_{film} + d_{WWC})(\delta_{film} + h_{WWC}) + \frac{\pi}{4} (\delta_{film} + d_{WWC})^2 \quad (5)$$

157 and the surface mole flow φ_{CO_2} [mol/(m² s)] as

$$\varphi_{CO_2} = \frac{\Delta N_{CO_2}}{A_{int}} \quad (6)$$

158 where d_{WWC} [m] is the diameter of the stainless steel cylinder in the reactor and the h_{WWC} [m] is the
 159 height of the stainless steel cylinder of the reactor.

160

161 The partial pressure of the carbon dioxide $P_{CO_2}^{WWC}$ [Pa] in the reactor is calculate according to the
 162 hypothesis of ideal mixture of ideal gas as

$$P_{CO_2}^{WWC} = y_{CO_2}^{WWC} P_{TOT}^{WWC} \quad (7)$$

163 where P_{TOT}^{WWC} [Pa] is the total pressure inside the reactor.

164

165 The concentration inside the reactor is different from the concentration measured by the CO₂ probe
 166 because between the chamber and the probe the condenser temperature is set to 13°C (lower than the
 167 temperature of reaction) which condenses a fraction of the water in the gas phase. Hence, the molar
 168 concentration at the inlet $y_{CO_2}^{WWC,in}$ [-] is calculate as

$$y_{CO_2}^{WWC,in} = y_{CO_2}^{bypass} \frac{1 - \frac{P_{H_2O}^{WWC}}{P_{TOT}^{WWC}}}{1 - \frac{P_{H_2O}^{cond.}}{P_{TOT}^{cond.}}} \quad (8)$$

169 and the molar concentration at the outlet $y_{CO_2}^{WWC,out}$ [-] of the reactor as

$$y_{CO_2}^{WWC,out} = y_{CO_2}^{WWC} \frac{1 - \frac{P_{H_2O}^{WWC}}{P_{TOT}^{WWC}}}{1 - \frac{P_{H_2O}^{cond.}}{P_{TOT}^{cond.}}} \quad (9)$$

170

171 where $P_{H_2O}^{WWC}$ [Pa] is the partial pressure of the water in the reactor, $P_{H_2O}^{cond.}$ [Pa] is the partial pressure of
 172 the water in the condenser, P_{TOT}^{WWC} [Pa] is the total pressure in the reactor and $P_{TOT}^{cond.}$ [Pa] is the total
 173 pressure in the condenser.

174

175 Because the CO₂ molar fraction is not constant in the reactor, the partial pressure in the reactor $P_{CO_2}^{gas}$ [Pa]
 176 is evaluated with the logarithmic mean

$$P_{CO_2}^{gas} = \frac{P_{CO_2}^{in} - P_{CO_2}^{out}}{\ln\left(\frac{P_{CO_2}^{in}}{P_{CO_2}^{out}}\right)} \quad (10)$$

177 where $P_{CO_2}^{in}$ [Pa] is the partial pressure of the CO₂ in the reactor inlet and $P_{CO_2}^{out}$ [Pa] is the partial pressure
 178 of the CO₂ in the reactor outlet.

179

180 According to Fick's law, the flux of carbon dioxide is proportional to the carbon dioxide concentration
 181 gradient in the diffusion direction. The proportionality factor is the diffusion coefficient of CO₂. Figure
 182 2 shows a schematic representation of the mass transfer process of a diffusing gas into a liquid. The
 183 absorption process of the CO₂ from a gas bulk with a partial pressure $P_{CO_2}^{gas}$ [Pa] into a liquid with a
 184 CO₂ concentration $C_{CO_2}^{liq}$ [mol/m³] can be described with the two film theory as reported in Figure 2a.

185

186 **Figure 2.** Left: the CO₂ partial pressure profile in the gas phase and the CO₂ concentration profile in the
 187 liquid phase according to the two film theory (Lewis and Whitman, 1924). Right: the CO₂ partial
 188 pressure profile in both the gas and liquid phase according to the two film theory (Lewis and Whitman,
 189 1924).

190 To uniform the driving force of the mass transfer phenomenon as dependent only on the partial pressure
 191 of the CO₂, the partial pressure of the CO₂ in liquid phase is calculated as

$$P_{CO_2} = H_{CO_2} C_{CO_2} \quad (11)$$

192 where H_{CO_2} [(Pa m³)/mol] is the partition coefficient and the C_{CO_2} [mol/m³] the concentration in the liquid
 193 phase. The partition coefficient in this work is taken as the Henry constant of the CO₂ in the solvent.

194

195 According to the two film theory (Lewis and Whitman, 1924), the flux of CO₂ can be described by the
 196 product between a mass transfer coefficient and the corresponding driving force expressed as the
 197 difference of the CO₂ partial pressure or CO₂ concentration. With this approach, the following
 198 expressions hold true:

$$\varphi_{CO_2}^G = k_G (P_{CO_2}^{gas} - P_{CO_2}^{int}) \quad (12)$$

$$\varphi_{CO_2}^L = k_{liq} (C_{CO_2}^{int} - C_{CO_2}^{liq}) = \frac{k_{liq}}{H_{CO_2}} (P_{CO_2}^{int} - P_{CO_2}^{liq}) = k'_{liq} (P_{CO_2}^{int} - P_{CO_2}^{liq}) \quad (13)$$

$$\varphi_{CO_2} = K_{ov} (P_{CO_2}^{gas} - P_{CO_2}^{liq}) \quad (14)$$

$$\varphi_{CO_2} = \varphi_{CO_2}^L = \varphi_{CO_2}^G \rightarrow \frac{1}{K_{ov}} = \frac{1}{k_G} + \frac{1}{k'_{liq}} \quad (15)$$

199 where $\varphi_{CO_2}^G$ [mol/(s m²)] is the CO₂ flux in gas phase, $\varphi_{CO_2}^L$ [mol/(s m²)] is the CO₂ flux in the liquid
 200 phase, φ_{CO_2} [mol/(s m²)] is the total CO₂ molar flux absorbed, K_{ov} is the overall mass transfer coefficient,
 201 expressed in [mol/(m²·sec·Pa)], $P_{CO_2}^{bulk}$, $P_{CO_2}^{int}$ and $P_{CO_2}^{liq}$ [Pa] are respectively the partial pressure of carbon
 202 dioxide in the bulk gas, at the interface and at the equilibrium in the liquid bulk. k_G [mol/(m²·sec·Pa)]
 203 and k'_{liq} [mol/(m²·sec·Pa)] are respectively the gas and liquid side mass transfer coefficient. As reported
 204 by Dugas *et al.* (Dugas, 2009), k'_{liq} is a function of both the physical diffusion of the reactants in the
 205 liquid and the effect of the chemical reaction.

206

207 Defining the enhancement factor E_{CO_2} [-] according to Swaaij and Versteeg (van Swaaij and Versteeg,
 208 1992) as

$$E_{CO_2} = \frac{(\varphi_{CO_2}^L)_{with\ chemical\ reactions}}{(\varphi_{CO_2}^L)_{without\ chemical\ reactions}} \quad (16)$$

209 where $(\varphi_{CO_2}^L)_{with\ chemical\ reactions}$ [mol/m²] is the surface flow of CO₂ with chemical reactions and
 210 $(\varphi_{CO_2}^L)_{without\ chemical\ reactions}$ [mol/m²] is the surface flow of CO₂ without chemical reactions, it is also
 211 valid the relation

$$k'_{liq} = \frac{k_{liq}^0 E_{CO_2}}{H_{CO_2}} \quad (17)$$

212 where k_{liq}^0 [m/s] is the liquid side mass transfer coefficient without chemical reactions calculated with
 213 the penetration theory of Higbie (Higbie, 1935) as proposed in (Gladis et al., 2017), and H_{CO_2} [(Pa
 214 m³)/mol] is the partition coefficient of the CO₂ in the solvent which correlates the concentration of CO₂
 215 at the equilibrium in the liquid phase with its partial pressure in the gas phase.

216

217 The K_{ov} is measured for different conditions by varying the reaction temperature, the ammonia
 218 concentration in the solvent and the CO₂ loading considering the relation reported in equation (14).
 219 Chosen a triplet of these parameters to be analyzed, a gas mixture with a known concentration of CO₂ is
 220 flowed in the reaction chamber where the φ_{CO_2} and the $P_{CO_2}^{gas}$ are calculated. This procedure is repeated
 221 for other five points with different concentrations of CO₂ in the gas. Matching the values of φ_{CO_2} and
 222 $P_{CO_2}^{gas}$ the result is a chart like in Figure 3 where the slope is represented by the K_{ov} and the interception
 223 with the x axes is the $P_{CO_2}^{liq}$. The approach used to measure the overall mass transfer coefficient neglects
 224 the ammonia slips in the reaction chamber. This assumption can be justified after a rate-based analysis
 225 of the reaction chamber in Aspen Plus with the Extended UNIQUAC thermodynamic model (Thomsen
 226 and Rasmussen, 1999). The results estimate an ammonia loss during the 30 minutes of the experiment
 227 lower than the 4% of the total ammonia present in the solvent for the case at 35°C, 15% of NH₃
 228 concentration and CO₂ loading of 0.2, which is the worst case in term of ammonia slip. On average the
 229 ammonia slip estimated for the cases is lower than the 1% of the total ammonia in the solvent.

Figure 3. CO_2 absorption flux as a function of CO_2 partial pressure in the reaction chamber for the case with 10% NH_3 , loading 0.6 and $25^\circ C$. The overall heat transfer coefficient K_{ov} is the slope of the line, the intercept is the partial pressure of the CO_2 in the liquid and the R^2 is the statistic index which determines the agreement between the interpolation line and the experimental data.

3. Characterization of the mass transfer in the Wetted Wall Column

The calculation of the enhancement factor with the equation (17) determines the effect of the reactions between the solvent and the CO_2 , so the values of the k'_{liq} and k^0_{liq} are needed. The gas side mass transfer coefficient k_G is calculated with a mass transfer correlation and the overall mass transfer coefficient K_{ov} is calculated from the experimental, so the value of k'_{liq} is calculated from the equation (15). The value of k^0_{liq} is calculated with the Higbie penetration theory (Higbie, 1935) as in the work by Gladis *et al.* (Gladis *et al.*, 2017) and presented in the following paragraphs. The enhancement factor describes the increment of absorption for the chemical reactions with respect to the pure physical absorption and, hence, also the kinetics of the reactions in the water phase. All the assumptions, correlations and values used for the calculations are described in this paragraph.

249 3.1. Determination of the physical properties of the solvent and the gas mixture

250 The physical properties of the species in the liquid and in the gas mixture are required in order to
251 determine the kinetic constant of the absorption reactions. The properties of interest are the diffusion
252 coefficients of the species in the liquid and the gas phases, the liquid phase properties and the partition
253 coefficient H_{CO_2} .

254

255 For what concern the gas diffusivity of the CO_2 in the gas phase the results are calculated with the
256 correlation of Fuller *et al.* (Fuller et al., 1966). The diffusion coefficient of the CO_2 , $D_{CO_2}^{sol}$ in the solvent
257 cannot be directly measured since the carbon dioxide is involved in chemical reaction in the diffusion
258 layer in the solvent. The solution is a predictive model that correlates a value measurable in a non-reactive
259 system with the value needed. The Stokes-Einstein relationship (Tarjus and Kivelson, 1995) exploits the
260 similarity of the behavior of different solvents depending on the rapport of the viscosities. The CO_2
261 diffusivity in water $D_{CO_2}^{H_2O}$ [m^2/s] is available by the correlation of Versteeg *et al.* (Versteeg and Van
262 Swaaij, 1988) in equation (18) as

$$D_{CO_2}^{H_2O} = 2.35 * 10^{-6} \exp\left(\frac{-2119}{T}\right) \quad (18)$$

263 so with the Stokes-Einstein relationship the diffusivity of the carbon dioxide in the solvent $D_{CO_2}^{sol}$ [m^2/s]
264 is computed as

$$D_{CO_2}^{sol} = D_{CO_2}^{H_2O} \left(\frac{\mu_{H_2O}}{\mu_{sol}}\right)^{0.8} \quad (19)$$

265 where T [K] is the temperature of the solvent, the μ_{sol} and μ_{H_2O} the viscosity of the solvent (measured)
266 and of the water (given by Refprop®).

267

268 The diffusivity of the NH_3 in the liquid phase $D_{\text{NH}_3}^{\text{sol}}$ [m^2/s] is calculated with the relation of Franck *et al.*
 269 (Frank et al., 1996) as

$$D_{\text{NH}_3}^{\text{sol}} = (1.65 + 2.47 x_{\text{NH}_3}) * 10^{-6} \exp\left(\frac{-1996.6}{T}\right) \quad (20)$$

270 where T [K] is the temperature of the solvent and x_{NH_3} [-] is the apparent molar concentration of
 271 ammonia.

272

273 The partition coefficient H_{CO_2} in aqueous ammonia solution can't be described by a simple correlation.
 274 In this work, as suggested by Darde in his PhD thesis (Darde, 2011), the value of H_{CO_2} is assumed equal
 275 to its value for the pure water. The experiments showed by Qin *et al.* (Qin et al., 2010) that the deviation
 276 between the values of H_{CO_2} for loaded solution of aqueous ammonia and pure water is up to 20%. Hence,
 277 since 20% is in agreement with the errors usually correlated to this kind of correlation, the assumption is
 278 reasonable. The correlation for the H_{CO_2} used in this work is embedded in the Extended-UNIQUAC
 279 thermodynamic model by Thomsen and Rasmussen (Thomsen and Rasmussen, 1999).

280 3.2. Determination of the gas side transfer constant k_G

281 The gas side transfer constant k_G is a function of the mass transfer in the gas phase. In the gas phase there
 282 is pure physical transport of CO_2 from the bulk of the gas to the interface due to a difference of partial
 283 pressure. Since the accuracy of the mass transfer correlation is usually very low, Gladis *et al.* (Gladis et
 284 al., 2017) calibrated the parameters of a dimensionless correlation of the Sherwood (Sh) number as a
 285 function of the Reynolds (Re) and Schmidt (Sc) number. The expression proposed by Pacheco (Pacheco,
 286 1998) propose the calculation of the Sherwood number Sh [-] as

$$Sh = C * Re^a Sc^a \left(\frac{d_H}{h_{WWC}}\right)^a \quad (21)$$

287 where d_H [m] is the hydraulic diameter (defined as the difference in diameter between outer annulus and
 288 the wetted wall column incorporating the liquid film) and h_{WWC} [m] the high of the Wetted Wall Column.
 289 The parameters C and a are fitted with the experiments of the SO₂ absorption with an aqueous solution
 290 of NaOH. In this conditions the absorption has instantaneous reaction, so all the resistance to the mass
 291 transfer is allocated in the gas layer. As shown by Gladis *et al.* (Gladis et al., 2017), the equation (21) fits
 292 the experimental data with an error lower than 10% which is a good result for a mass transfer correlation.
 293 After the fitting process and the constants calibration the equation (21) can be written as

$$\frac{k_G d_H R T}{D_{CO_2}^{gas}} = 3.61 * \left(\frac{d_H v_{gas} \rho_{gas}}{\mu_{gas}} \right)^{0.59} \left(\frac{\mu_{gas}}{\rho_{gas} D_{CO_2}^{gas}} \right)^{0.59} \left(\frac{d_H}{h_{WWC}} \right)^{0.59} \quad (22)$$

294 where $D_{CO_2}^{gas}$ [m²/s] is the diffusivity of the CO₂ in the gas mixture, R [J/(K mol)] the universal gas
 295 constant, T [K] the gas temperature, v_{gas} [m/s] the gas velocity, μ_{gas} [Pa s] the gas viscosity and ρ_{gas}
 296 [kg/m³] the gas density.

297 The relation in equation (22) allows to calculate the k_G which is needed for the calculation of the k'_{liq} .

298 3.3. Determination of the gas side transfer constant k_{liq}^0

299 The physical liquid mass transfer coefficient k_{liq}^0 [m/s] is the mass transfer coefficient in the liquid phase
 300 in absence of chemical reactions. Since it is a physical property of the solvent, its expression derives
 301 from the momentum balance, so k_{liq}^0 can be determined with the theoretical expression based on the
 302 penetration theory of Higbie as (Higbie, 1935)

$$k_{liq}^0 = 2 \sqrt{\frac{D_{CO_2}^{sol}}{\pi \tau}} \quad (23)$$

303 where τ [s] is the contact time between the liquid and the gas calculated as

$$\tau = 3 h_{WWC} \left(\frac{\rho_{liq} g}{\mu_{liq}} \right)^{-\frac{1}{3}} \left(\frac{3 V_{liq}}{L} \right)^{-\frac{2}{3}} \quad (24)$$

where L [m] is the perimeter of the Wetted Wall Column and the V_{liq} [m³/s] the volumetric flow of the liquid.

306

The k'_{liq} is a function of both the physical diffusion of the reactants in the liquid and the effect of the chemical reaction while the k^0_{liq} is a function of only the physical diffusion. Hence, it indicates how the chemical reaction increases the absorption with respect of pure physical diffusion. The number defined to evaluate this contribution is the enhancement factor that can be calculated as:

$$E_{CO_2} = \frac{(\varphi^L_{CO_2})_{with\ chemical\ reactions}}{(\varphi^L_{CO_2})_{without\ chemical\ reactions}} = \frac{k'_{liq} H_{CO_2}}{k^0_{liq}} \quad (25)$$

The enhancement factor quantify how the chemical reactions enhance the adsorption rate of the process. The computation of the kinetic constant of every single reaction involved in the absorption process is described in the next paragraph after modelling the chemistry of the process and the hypothesis that describes the process in this conditions.

4. Rate of absorption and kinetic constant

During the absorption of CO₂ in to aqueous ammonia there are three main reactions that happen in the liquid interface. The reactions are: the carbonic acid formation (R1), the bicarbonate formation (R2) and the carbamate formation (R3). The aim is the characterization of the reaction rate of each of these reactions and characterize the overall kinetic of the absorption.

320 According to Blauwhoff *et al.* (Blauwhoff, 1983), reaction (R1) is considered to have a negligible
321 contribution to the overall rate of absorption as this reaction is very slow compared to the other ones.

322

323 The reaction rate of the reaction (R2) $r_{CO_2-OH^-}$ [mol/(m³ s)] is described with an experimental study by
324 Pinsent *et al.* (B. R. W. Pinsent *et al.*, 1956). The results report kinetics of the second order with an
325 Arrhenius expression of the kinetic constant:

$$r_{CO_2-OH^-} = k_{OH^-} C_{CO_2} C_{OH^-} \quad \text{with} \quad k_{OH^-} = 4.2 * 10^{13} \exp\left(\frac{-2895}{T}\right) \quad (26)$$

326 where k_i [1/s] is the kinetic constant for the component and C_i [mol/m³] is the concentration of
327 component i .

328 The reaction rate of the reaction (R3) is the object of this work. The equations used to characterize the
329 kinetic of the (R3) are presented in equation (27) as

$$r_{CO_2-NH_3} = k_{NH_3} C_{CO_2} C_{NH_3}^\gamma \quad \text{with} \quad k_{NH_3} = A * \exp\left(-\frac{E_A}{RT}\right) \quad (27)$$

330 where E_A [J/mol] is the activation energy, A [m³??/(mol?? s)] pre-exponential factor of the Arrhenius
331 constant and γ a coefficient experimentally fitted.

332

333 The equations used to describe the phenomenon do not take in account any reaction mechanism contrary
334 to Darde *et al.* (Darde *et al.*, 2011) in order to simplify the future implementation of the model in a
335 process simulation software. Indeed, considering for instance the zwitter ion mechanism as in the Darde
336 *et al.* (Darde *et al.*, 2011) paper, the kinetic model assume an expression that can not be implemented in
337 Aspen Plus ®.

338 Defined the kinetic constants for the two reaction involved in the CO₂ absorption, equation (28) defines
339 an overall kinetic rate constant k_{ov} [1/s] which represents the sum of the contributions of the reactions
340 (R2) and (R3) as

$$k_{ov} = \frac{r_{CO_2-NH_3}}{C_{CO_2}} + \frac{r_{CO_2-OH^-}}{C_{CO_2}} = k_{NH_3} C_{NH_3}^\gamma + k_{OH^-} C_{OH^-} \quad (28)$$

341 As proposed by Darde *et al.* (Darde et al., 2011), if the absorption reactions are in a particular regime
 342 called pseudo-first order regime, there is a direct relation between the enhancement factor and the k_{ov} .
 343 The pseudo-first order regime is a condition where the concentration of one of the reactants (in this case
 344 the ammonia) in the reactive layer of the liquid film is in excess, so its concentration is considered
 345 constant in all the liquid film. In order to verify the pseudo-first order regime, the value of the Hatta
 346 number Ha defined as

$$Ha = \frac{\sqrt{k_{ov} D_{CO_2}^{sol}}}{k_{CO_2}^{0Liq}} \quad (29)$$

347 must be in a range between 3 and a value around one fifth of E_∞

$$3 < Ha \ll E_\infty \quad (30)$$

348 with E_∞ the limit for instantaneous reactions defined as

$$E_\infty = 1 + \frac{D_{NH_3}^{sol} C_{NH_3}^{bulk}}{2D_{CO_2}^{sol} C_{CO_2}^{int}} \quad (31)$$

349 where $D_{NH_3}^{sol}$ [m²/s] the diffusivity of the ammonia in the liquid, $C_{NH_3}^{bulk}$ [mol/m³] the ammonia
 350 concentration in the liquid bulk, $D_{CO_2}^{sol}$ [m²/s] the diffusivity of the CO₂ in the liquid and $C_{CO_2}^{int}$ [mol/m³]
 351 the concentration of CO₂ at the interface.

352

353 In pseudo-first order regime the Hatta number Ha and the enhancement factor E_{CO_2} are bound by the
 354 following relation

$$E_{CO_2} = \frac{(\varphi_{CO_2})_{with\ reactions}}{(\varphi_{CO_2})_{without\ reactions}} = \frac{k'_{Liq} H_{CO_2}}{k_{Liq}^0} = \frac{Ha}{\tanh(Ha)} \quad (32)$$

Hence, if the pseudo-first order regime is respected, there is a relation between the enhancement factor and the Hatta number. Since the enhancement factor is measurable with the WWC, the Hatta number is known and consequently also the k_{NH_3} .

5. Error propagation analysis

The passages for the overall mass transfer coefficient are algebraic. The propagation of the instrumental uncertainty $U(y)$ of the dimension $y = f(x_1, x_2, \dots, x_n)$ is calculated with the formula in equation (33) as explained in the text book by Jhon R. Taylor (Taylor, 2000)

$$U(y) = \sqrt{\sum_{i=1}^N \left(\frac{\partial f}{\partial x_i} \right)^2 * (U(x_i))^2} \quad (33)$$

where $U(x_i)$ is the absolute uncertainty of the dimension x_i . The equation (33) calculates the absolute uncertainty for each value.

The overall mass transfer coefficient K_{ov} is the result of the linear regression of the chart presented in Figure 3, where there are the molar flow of CO₂ φ_{CO_2} on the y axis and the partial pressure of CO₂ $P_{CO_2}^{gas}$ on the x axis. The formula of the total uncertainty related to the K_{ov} , $U(K_{ov})$, is described in equations (34) (35) from the text book by Jhon R. Taylor (Taylor, 2000)

$$U(\varphi_{CO_2})_{equivalent} = \sqrt{U(\varphi_{CO_2})^2 + [K_{ov} * U(P_{CO_2}^{gas})]^2} \quad (34)$$

$$U(K_{ov}) = U(\varphi_{CO_2})_{equivalent} * \sqrt{\frac{N_{data}}{N_{data} * \sum_1^{N_{data}} (P_{CO_2,i}^{gas}) - [\sum_1^{N_{data}} (P_{CO_2,i}^{gas})]^2}} \quad (35)$$

where N_{data} is the number of points involved in the linear regression, $U(\varphi_{CO_2})$ the total uncertainty of the molar flow of CO₂, $U(P_{CO_2}^{gas})$ the total uncertainty of the CO₂ partial pressure and $U(\varphi_{CO_2})_{equivalent}$

371 a parameters which represents the sum of the uncertainties $U(\varphi_{CO_2})$ and $U(P_{CO_2}^{gas})$. The overall mass
372 transfer coefficient is calculated directly from the experimental data, since there are no assumptions on
373 physical properties or heat and mass transfer correlations.

374
375 The k'_{liq} is computed from the K_{ov} value. The passages that leads the calculation of the k'_{liq} from the
376 K_{ov} , as explained in the paragraph 3, use a lot of correlations for the mass transfer coefficients and the
377 physical properties of the solvents and the gas phase. These assumptions have an error that is propagated
378 like the other measures with the equation (34). Mainly the correlations with the higher errors are the
379 correlation for the mass transfer in the gas phase (10%) and the correlation for the partition coefficient
380 of the CO_2 (20% as reported by Qin *et al.* (Qin et al., 2010)). As it will be shown by the paper these two
381 correlation have the stronger impact in the error on the kinetic constant of the reaction (R3) k_{NH_3} .

382 **6. Results and discussion**

383 The K_{ov} is measured for a range of temperatures between 15°C and 35°C, the ammonia concentration
384 concentrations between 5% and 15% wt. and CO_2 loadings between 0.2 and 0.6. The intervals of value
385 investigated were selected considering the typical conditions of the solvent in an absorption column in a
386 post-combustion plant with aqueous ammonia solutions. The conditions are reported in many works on
387 the Chilled Ammonia Process (Valenti et al., 2012)(Valenti et al., 2012)(Svendsen et al., 2011)(Bai and
388 Yeh, 1997)(Darde et al., 2012)(Lillia et al., 2016)(B R W Pinsent et al., 1956)(Wang et al., 2011)(Li et
389 al., 2015). After the K_{ov} measurement, the fitting of the kinetic model with all the data in pseudo-first
390 order regime determines the rate of the reaction (R3). The error analysis is important to compare the
391 dispersion of the experimental values with the errors of the measurements and, if the dispersion is lower
392 than the error, state that the measurements are reliable with the hypothesis of the calculations.

393 6.1. Liquid side mass transfer coefficient

394 Figure 4 presents the results of the K_{ov} for all the analyzed cases. K_{ov} decreases with the loading of the
395 solvent and the initial ammonia concentration. The explanation is the reduction of the free ammonia in
396 the bulk liquid. Indeed, increasing the loading, the ammonia in the liquid reacts with CO_2 , forming
397 carbamate and ammonium ions. As shown by equation (27) the rate of reaction (R3) is dependent on the
398 free ammonia concentration in the bulk which is reduced due to reaction.

399

400 The third variable analyzed is the temperature. As the Arrhenius expression of the kinetic constant
401 describes, there is an exponential dependence on the temperature following the Maxwell Boltzmann
402 distribution of the kinetic energy. Figure 4 shows that rising the temperature, the K_{ov} increases.
403 Moreover, as suggested by the exponential law, the difference between 15°C and 25°C is lower than the
404 difference between 25°C and 35°C.

405

406 Another interesting behavior of the K_{ov} is observed close to CO_2 saturation. At high loading, all the
407 points collapse close to each other. This phenomenon is also explained by equation (27): at high loading,
408 the free ammonia concentration is low and consequently the impact of its initial concentration and the
409 temperature of reaction decreases. The overall mass transfer constant K_{ov} has values generally in
410 agreement with Darde *et al.* (Darde et al., 2011) and Puxty *et al.* (Puxty et al., 2010). Moreover, the
411 trends of the results in this work on loading are similar at every ammonia concentration as suggested by
412 the theory contrary to the other works.

413

414 Figure 5 shows the results of the liquid side mass transfer coefficient k'_{liq} . The results follow the same
415 trends as the overall mass transfer coefficient in Figure 4. Indeed the value of the gas side mass transfer
416 k_G reduces the K_{ov} with respect to the k'_{liq} of a value between 8% and 15%, higher when the absorption

417 reactions are fast and vice versa when absorption reactions are slower, so it does not change a lot the
 418 overall trend. Compared with the results of Darde *et al.* (Darde et al., 2011), the values reported here are
 419 generally in agreement. Figure 6 and Figure 7 compare in the same chart the results obtained by Darde
 420 *et al.* (Darde et al., 2011) and Puxty *et al.* (Puxty et al., 2010) with the results obtained in this work.

421
 422 The relative errors of the K_{ov} and the k'_{liq} are between the 2% and the 3%. The relative error of the k'_{liq}
 423 is low despite the applied relation for the mass transport has an error of 10%. This is because the gas
 424 resistance to the mass transfer is an order of magnitude lower than the liquid mass transfer. Hence, for
 425 the theory of the error propagation the relative error of the k'_{liq} remains almost the same as for the K_{ov} .
 426 In brief, the wetted wall column is a reliable and accurate method that measure the CO₂ transport from
 427 the bulk gas phase to the liquid.

428
 429 **Figure 4.** Overall mass transfer coefficient as a function of the CO₂ loading for 5%, 10% 15% of NH₃
 430 concentration at 15°C, 25°C and 35°C.

431

432 **Figure 5.** Liquid side mass transfer coefficient as a function of the CO₂ loading for 5%, 10% 15% of NH₃
 433 concentration at 15°C, 25°C and 35°C.

434

435 **Figure 6.** Comparison of the overall mass transfer coefficient results between Puxty *et al.* and the present
 436 work

Figure 7. Comparison of the liquid side mass transfer coefficient results between Darde *et al.* and the present work

6.2. Chemical reaction rate between CO₂ and ammonia and error analysis

The Extended-UNIQUAC thermodynamic model by Thomsen and Rasmussen (Thomsen and Rasmussen, 1999) allows an accurate calculation of the speciation in the liquid phase at the relevant conditions, so it allows also the fitting of the data measured with loaded solvents.

The cases in pseudo-first order regime are in an operative condition where there is an excess of free ammonia in the reaction layer, so the ammonia concentration in the reactive layer can be approximated

451 as constant and equal to the bulk concentration. This condition is valid at high ammonia concentrations
452 and/or at low CO₂ loadings and consequently not all the cases analyzed respect this assumption. By
453 calculating the k_{NH_3} and its error for every case in pseudo-first order regime, the parameters presented
454 in equation (27) are fitted. The first parameter γ , which is the exponent of the ammonia concentration, is
455 fitted minimizing the dispersion of the k_{NH_3} found at the same temperature but at different ammonia
456 conditions and CO₂ loadings. With the ammonia concentration exponent $\gamma = 1.89$ as Figure 8 shows, the
457 dispersion is inside the uncertainty range, so all the data are acceptable. Further, the pre-exponential
458 factor and the activation energy are fitted in order to follow the mean values at every considered
459 temperature. The result shows an R^2 factor really close to 1 that means a very good agreement between
460 the experimental data and the Arrhenius law. Equation (36) reports the model after the data fitting.

461

462

463 **Figure 8.** The filled circles are the experimental values of the k_{NH_3} at every temperature for all the cases
 464 in pseudo-first order regime and with the filled diamonds the mean value at every temperature. The dotted
 465 yellow line is the regression with the Arrhenius law expressed in equation (27). The black dotted lines
 466 are the upper and the lower limit of the mean value of k_{NH_3} due to the absolute errors of the measurement.

$$r_{CO_2-NH_3} = k_{NH_3} C_{CO_2} C_{NH_3}^{1.89} \quad \text{with} \quad k_{NH_3} = 1.41 * 10^8 \frac{\text{mol}}{\text{m}^3 \text{s}} \exp\left(-\frac{60680 \frac{\text{J}}{\text{mol}}}{RT}\right) \quad (36)$$

467 The aim of this work is a model to be implemented in a process simulation software. Since the partition
 468 coefficient H_{CO_2} has a strong dependence on the value of the kinetic constant k_{NH_3} , the partition
 469 coefficient correlations used in the process simulation software must be the same as the correlations used
 470 to fit the model.

471

472 The value of the kinetic constant of the reaction (R3) k_{NH_3} is calculated with its error following the
 473 procedure of paragraph 5. Despite the error of the overall mass transfer coefficient is low (around 3%)

474 the error of the k_{NH_3} is around 40%. The main reason is due to the error in the partition coefficient. As
475 reported by Qin *et al.* (Qin et al., 2010) the partition coefficient of an aqueous ammonia solution is close
476 to the partition coefficient of pure water with an error up to 20%. Hence, the propagation of this error
477 brings the relative error of the k_{NH_3} an order of magnitude higher. Moreover, this results shows that the
478 value of the k_{NH_3} has a strong dependence to the value of the partition coefficient H_{CO_2} , so changing the
479 assumption or the correlation to calculate it, the value of the k_{NH_3} can change a lot.

480 6.3. Comparison with the literature

481 In literature there are not many kinetic models of the reaction rate of the reaction (R3) (Lillia et al., 2016).
482 Moreover, as reported by Lillia *et al.* (Lillia et al., 2016), the kinetic constants published are often not in
483 agreement with each other. The different works determine the rate of reactions with different
484 experiments, at different conditions of reactant concentrations and with different models. The works of
485 Pinsent *et al.* (B R W Pinsent et al., 1956), Puxty *et al.* (Puxty et al., 2010), Jilvero *et al.* (Jilvero et al.,
486 2014) and Darde *et al.* (Darde et al., 2011) illustrate this.

487
488 Pinsent *et al.* (B R W Pinsent et al., 1956) studied the kinetics of reaction (R3) by the rapid thermal
489 method with an ammonia concentration between 0.027 mol/dm³ and 0.19 mol/ dm³.

490
491 Puxty *et al.* (Puxty et al., 2010) studied the kinetics of reaction (R3) by measuring the rate of CO₂
492 absorption into a falling thin film using a wetted wall column for aqueous ammonia between 0.6 mol/
493 dm³ and 6 mol/ dm³ (1% and 10% wt.), 5–20 °C (278-293 K) and initial thin liquid film CO₂ loadings
494 between 0 mol_{CO2}/mol_{NH3} and 0.8 mol_{CO2}/mol_{NH3}.

495

496 Jilvero et al. (Jilvero et al., 2014) studied the kinetics of reaction (R3) by a different approach with respect
 497 to the works cited previously. In their work Jilvero *et al.* implemented an absorption column in Aspen
 498 Plus taking all the design parameters from the Munmorah Aqueous Ammonia pilot (Yu et al., 2011).
 499 Consequently, they fit the kinetic parameters of reaction (R3) to the experimental data from the pilot
 500 plant, arriving at different Arrhenius parameters than the other works.

501

502 These three works (Pinsent *et al.* (B R W Pinsent et al., 1956), Puxty *et al.* (Puxty et al., 2010), Jilvero
 503 *et al.* (Jilvero et al., 2014)) propose a rate of reaction of the second-order as in equation (37), which is
 504 the equation (27) where the dependence on the ammonia concentration is linear ($\gamma = 1$).

$$r_{CO_2-NH_3} = k_{NH_3} C_{CO_2} C_{NH_3} \quad \text{with} \quad k_{NH_3} = A * \exp\left(-\frac{E_A}{RT}\right) \quad (37)$$

505 Darde *et al.* (Darde et al., 2011) studied the kinetics of the reaction (R3) by measuring the rate of CO₂
 506 absorption into a falling thin film using a wetted wall column for aqueous ammonia between 1% and
 507 10%, 5–20 °C (278-293 K) and initial thin liquid film CO₂ loadings between 0 mol_{CO2}/mol_{NH3} and 0.8
 508 mol_{CO2}/mol_{NH3}. Contrary to Puxty *et al.*, the rate of the reaction (R3) is modeled considering the zwitter-
 509 ion mechanism according to Versteeg *et al.* (Derks and Versteeg, 2009). The zwitter-ion mechanism is a
 510 two step mechanism (R4, R5) of the reaction (R3) in the water phase

511 where B is a species that can be protonized and split the zwitter-ion ($NH_3^+ COO^-$). In the system H₂O-
 512 NH₃-CO₂, B can be H₂O or ammonia, so the rate of the reaction (R3) can be written as follows in
 513 equations (38)-(39):

$$r_{CO_2-NH_3} = k_{NH_3} C_{CO_2} C_{NH_3} - k_{-1} C_{NH_3^+ COO^-} = C_{NH_3^+ COO^-} \sum_{B_i} k_B C_B \approx C_{NH_3^+ COO^-} (k_{H_2O} C_{H_2O} + k_{NH_3} C_{NH_3}) \quad (38)$$

$$r_{CO_2-NH_3} = \frac{C_{CO_2} C_{NH_3}}{\frac{1}{k_2} + \frac{k_{-1}}{k_2} \left(\frac{1}{k_{H_2O} C_{H_2O} + k_{NH_3} C_{NH_3}} \right)} \quad (39)$$

514 The zwitter-ion mechanism returns the most scientific expression for the rate of reaction despite his
 515 complexity represents often a problem for its implementation in a process simulation software. The more
 516 simple equation (27) used in this work does not explicit the contribute of the water concentration in the
 517 solvent but it considers its effect calibrating the exponent γ with the experimental data. Moreover, water
 518 as reported by Darde *et al.* (Darde et al., 2011) has a secondary effect with respect to the ammonia
 519 concentration since its kinetic constant has a very low value. In addition, the concentration of water is
 520 always very high and does not change too much in the standard operative conditions. Hence, the
 521 approximation introduced would not be very influent in computational terms.

522

523 A novelty of this work is in the calculation of the reaction rate of the reaction (R3). The first difference
 524 between this work and the other works are the data considered to fit the model. Indeed, the other works
 525 always propose a model fitted only to the data measured with unloaded solvents. The advantage of
 526 unloaded solutions is that the free ammonia concentration in the bulk is easy to calculate despite unloaded
 527 condition of the solvent are never present in an absorption column. Hence, even if the model fits the data
 528 perfectly, there is no experimental evidence that the model works also at loaded conditions.

529

530 The apparent kinetic constant $k_{app}^{CO_2-NH_3}$ [1/s] represents the kinetics of the reaction (R3) without
 531 considering the effect of the CO_2 concentration. This constant is defined in order to compare the results
 532 among the cited works and the present, since the models in every work are different. $k_{app}^{CO_2-NH_3}$ is defined
 533 as

$$k_{app}^{CO_2-NH_3} = k_{ov} - k_{OH^-}C_{OH^-} \quad (40)$$

534 which is the overall CO₂ absorption reaction, represented by the k_{ov} [1/s], minus the contribution of the
 535 reaction (R2) expressed as $k_{OH^-}C_{OH^-}$ where k_{OH^-} [m³/(mol s)] is the kinetic constant of the reaction
 536 (R2) and C_{OH^-} [mol/ m³] the concentration of the OH⁻ ions.

537

538 Figure 9 show the apparent kinetic constant of the four cited works at 15°C, 25°C and 35°C as a function
 539 of the free ammonia concentration in the bulk.

Figure 9. Apparent kinetic constants for the four model cited from the literature and the model presented in this work as a function of the free ammonia concentration in the liquid for three different temperatures (15°C, 25°C and 35°C). The circles allow to understand the range of concentration at which every model has been calibrated and highlight that the model of the present work intercept the models from the literature close to the range of calibration.

540 The first three authors propose a linear dependence of the apparent kinetic constant with respect to the
541 free ammonia concentration. Darde *et al.* (Darde et al., 2011), considering the mechanism of reaction,
542 show a parabolic dependence like in the present work. Hence, the parabolic dependence by the free
543 ammonia concentration in the liquid is supported also by the hypothesis of the zwitter-ion mechanism
544 for the reaction (R3).

545

546 Taking into consideration the range of concentrations of the ammonia analyzed in the different works,
547 the apparent kinetic constant proposed in the present work intercepts the models around the range of
548 values at which they were fitted. This evidence suggests that the reaction (R3) has not a kinetics of the
549 second order as presented in equation (36) but a parabolic dependence on the ammonia concentration.

550

551 Finally, the $k_{app}^{CO_2-NH_3}$ values by Darde *et al.* (Darde et al., 2011) are not the same as in this work because
552 the mass transfer correlation used to calculate the gas mass transfer coefficient k_G and the correlation
553 used to calculate the partition coefficient H_{CO_2} are different. Moreover, in this work the model is fitted
554 with data at loaded conditions and not only at unloaded conditions like in the work by Darde *et al.* (Darde
555 et al., 2011).

556 7. Conclusions

557 In the present work, different cases are investigated in the region defined by temperatures from 15°C to
558 35°C, NH₃ concentrations from 5% to 15% and CO₂ loadings from 0.2 to 0.6 which are the typical solvent
559 conditions in absorption columns for a total of 27 different combinations of parameters. The following
560 conclusions are made:

- 561 • Measured K_{ov} values follow the trends described by the equations chosen to model the absorption
562 reactions.

- A model for the rate of reaction, valid for the temperature conditions, CO₂ loading, and ammonia concentration examined in this work was developed. The model uses an Arrhenius constant with a pre-exponential factor of $1.41 \cdot 10^8$ [mol/(m³s)] and an activation energy of 60680 [J/mol]. It has a linear dependence on the CO₂ concentration and a dependence on the NH₃ concentration with an exponent $\gamma = 1.89$.
- The exponent $\gamma = 1.89$ is close to 2, which is the exponent suggested by the stoichiometry of the reaction of the carbamate formation and the mechanism of reaction proposed by Versteeg *et al.* (Derks and Versteeg, 2009), so there is a theoretic support for the results.
- The error on the measurement of the kinetic constant k_{NH_3} is mainly due to the error on the partition coefficient, so a relation of the partition coefficient with a lower error can improve the accuracy of k_{NH_3} . However, a reactive system does not permit a direct evaluation of a partition coefficient and this is why there are no accurate relations to evaluate the partition coefficient for the ternary system H₂O-CO₂-NH₃.
- K_{ov} values measured near conditions already investigated in literature are in agreement with the values available from other sources.

A future work will be the test of the proposed kinetic relation in an Aspen simulation of an absorption column and validate the results with a pilot plant in order to determine if the approach used can be reliable for other solvents and other conditions.

Nomenclature:

Acronyms

WWC	Wetted Wall Column
WWC,in	Wetted Wall Column inlet
WWC, out	Wetted Wall Column outlet
Cond.	Condenser

588	Liq.	Liquid phase
589	Gas	Gas phase
590	Bulk	Bulk layer
591	<i>Symbols</i>	
592	a	exponent used in Sherwood correlation [-]
593	A	pre-exponential factor of the Arrhenius constant [$\text{m}^3/(\text{mol s})$]
594	A_{int}	interfacial area in the wetted wall column [m^2]
595	C	constant in Sherwood correlation [-]
596	C_i^j	concentration of component i at position j [mol/m^3]
597	D_i^j	diffusion coefficient of compound i in media j [m^2/s]
598	d_H	hydraulic diameter [m]
599	E_A	activation energy [J/mol]
600	E_{CO_2}	enhancement factor [-]
601	g	gravity acceleration constant [m/s^2]
602	h_{WWC}	height of the wetted wall column [m]
603	H_{CO_2}	partition coefficient of CO_2 [$(\text{Pa m}^3)/\text{mol}$]
604	Ha	Hatta number [-]
605	K_{ov}	overall mass transfer coefficient for the CO_2 transport [$\text{mol}/(\text{Pa m}^2 \text{ s})$]
606	k_i	kinetic constant for the component i [$\text{m}^3/(\text{mol s})$]
607	k_{ov}	overall kinetic constant [$1/\text{s}$]
608	k_G	gas side mass transfer coefficient [$\text{mol}/(\text{Pa m}^2 \text{ s})$]
609	k_{liq}	liquid side mass transfer coefficient related to the difference of concentrations [m/s]
610	k'_{liq}	liquid side mass transfer coefficient related to the difference of partial pressure [$\text{mol}/(\text{Pa m}^2 \text{ s})$]
611	k_{liq}^0	liquid side mass transfer coefficient without chemical reactions [m/s]
612	k_{app}^{i-j}	apparent kinetic constant of the reaction between i and j [$1/\text{s}$]
613	L	perimeter of the wetted wall column [m]
614	N_{data}	number of data [-]
615	N_i^j	mole flow of component i at position j [mol/s]
616	P_i^j	partial pressure of component i at position j [mol/s]
617	R	universal gas constant [$\text{J}/(\text{K mol})$]
618	Re	Reynold number [-]
619	r_{i-j}	rate of reaction between components i and j [$\text{mol}/(\text{m}^3 \text{ s})$]
620	Sc	Schmidt number [-]

621	Sh	Sherwood number [-]
622	T	temperature [K]
623	$U(i)$	uncertainty of the dimension i
624	v_{gas}	gas velocity [m/s]
625	V_{gas}	liquid volume flow [m ³ /s]
626	x_i^j	mole fraction of component i at position j in the liquid phase[-]
627	y_i^j	mole fraction of component i at position j in the gas phase [-]
628	<i>Greek symbols</i>	
629	δ_{film}	liquid film thickness [m]
630	μ_L	viscosity [Pa s]
631	ρ_L	density [kg/m ³]
632	τ	contact time [s]
633	φ_i^j	molar surface flow of the specie i in media j [mol/(m ² s)]

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635 Bibliography

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